

86. (NEW) A CVD precursor composition for forming a thin film dielectric on a substrate, such precursor composition including a metalloamide source reagent compound selected from the group consisting of: $Zr(NMe_2)_2(NPr_2)_2$, and $Zr(NEt_2)_2(NPr_2)_2$.

Remarks

Affirmation of Prior Provisional Election and Cancellation of Withdrawn Claims

Applicant hereby affirms the prior provisional election of Group I, Species I(a) to claims 1-12, 16-18 and 37 made in applicant's May 2, 2002 Response in Paper No. 6 in the patent application referenced hereinabove.

Applicant further affirms that during a telephone call between the undersigned agent and Examiner Kielin, on July 1, 2002, applicant agreed to the removal of elected claims 17 and 18 from species group I(a) as having been inadvertently grouped with species I(a), but properly belonging with species I(c).

Consistent with the Examiner's finalization of the restriction and election of species requirement and withdrawal of claims 13-15, 17-36 and 38-85 in the July 9, 2002 Office Action, claims 13-15, 17-36 and 38-85 have been cancelled herein.

Such cancellation is with express reservation of the right to file divisional application(s) directed to the subject matter thereof, during the pendency of the present application, or during the pendency of a further divisional or continuing application based on and claiming the priority of the present application.

Information Disclosure Statement

In the July 9, 2002 Office Action in the present application, the Office indicated that applicant's Information Disclosure Statement, as filed on July 17, 2002 failed to comply with 37 C.F.R. § 1.98(a)(2), which requires a legible copy of each U.S. and foreign patent; each publication or that portion which caused it to be listed; and all other information or that portion which caused it to be listed. More specifically, applicant failed to provide a copy of each of the following patent applications with the July 17, 2002 Information Disclosure Statement submission:

No. 09/414,133	In the name of Thomas H. Baum, et al.,	having a U.S. filing date of 10/7/99;
No. 07/927,134	In the name of Peter S. Kirlin, et al.,	having a U.S. filing date of 8/7/92;
No. 07/615,303	In the name of Duncan W. Brown et al.,	having a U.S. filing date of 11/19/90; and
No. 07/549,389	In the name of Peter S. Kirlin, et al.,	having a U.S. filing date of 7/6/90

In response, applicant provides herein, in Appendix D, a legible copy of U.S. patent application no.s, 07/927,134, 07/615,303, and 07/549,389, as well as U.S. patent no. 6,399,208 in place of U.S. patent application no. 09/414,133 as such patent application has granted. A PTO-1449 replacement "sheet 1", is enclosed herein in Appendix E, which servers to add the first named inventor in line item AR, and to add U.S. patent no. 6,399,208 in line item AF.

Accordingly, please replace applicant's originally submitted PTO-1449 "sheet 1" with the enclosed PTO-1449 "replacement sheet 1".

Based on the enclosed patent applications (copy) and U.S. patent (copy) documents provided herein in Appendix D, applicant's information disclosure statement, filed on July 17, 2001 is in compliance with 37 C.F.R. § 1.98(a)(2).

Objection to Drawings Under 37CFR § 1.84(p)(5)

Figure 1 in the present application was objected to based on MPEP § 608.02(g), because the figure, although illustrating only that which is old, fails to indicate a legend such as --Prior Art--.

In response, applicant submits herein, in accordance with 37 CFR § 1.121, under separate cover, a replacement sheet "Figure 1", having indicated in permanent, red ink, the legend "Prior Art".

Figures 2A, 2B, 7A and 7B were objected to as failing to comply under 37CFR § 1.84(p)(5) because they include reference sign(s) not mentioned in the description. Specifically, an indication as to what each of the "G" numbers represent is required for understanding of the figures.

In response applicant has amended herein paragraph 1, page 27 and paragraph 1, page 30 to identify the "G" numbers as identifiers for the various experiments run to obtain gate dielectric thin films.

Based on the foregoing, Figures 1-11 are now in compliance with 37CFR § 1.84(p)(5) and applicant respectfully requests that the objection of such Figures be withdrawn.

Current Status of Claims

Claims 1-5, 8-12, 16, 37 and 86 are pending.

Claims 1, 2, 3, 6, 9 and 37 have been amended.

Claims 6, 7, 13-15, 17-36 and 38-85 have been cancelled.

Claim 86 is new and fully supported by the present specification on page 14, first full paragraph and thus introduces no new matter.

Claims 1 and 37 have been amended herein to include a limitation, which identifies "x" as between 2 and 5, where x was previously identified in the instant application as the oxidation state on metal "M". Specifically claim 1 has been amended to read as follows:

A CVD precursor composition for forming a thin film dielectric on a substrate, such precursor composition including at least one metalloamide source reagent compound of the formula:



wherein M is selected from the group consisting of: Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti, Al; N is nitrogen each of R¹ and R² is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, C₁-C₈ perfluoroalkyl, and alkylsilyl; and x is from 2 to 5, with the proviso that at least two of x are different.

According to MPEP 2163.07(a) Inherent Function, Theory, or Advantage

By disclosing in a patent application a device that inherently performs a function or has a property, operates according to a theory or has an advantage, a patent application necessarily discloses that function, theory or advantage, even though it says nothing explicit concerning it. The application may later be amended to recite the function, theory or advantage without introducing prohibited new matter.

As "x" has been clearly defined in the instant specification as the oxidation state of metal "M" "x" is inherently equivalent to the stable oxidation states available to metal "M".

Applicant has amended claims 1 and 37 in the present application to include a range of oxidation states present in the metal species identified therein. Table 1, below, outlines the cited metals

useful in the present invention and disclosed in the present application on Page 6, final paragraph and on Page 7, first paragraph, and provides stable oxidation states based on the **Periodic Table of Elements**, which is documentation readily available to skilled artisans. Enclosed herein in Appendix F is a copy of such **Periodic Table of Elements** from which the stable oxidation states data originated. Such information is well known to skilled artisans.

Table 1: Metals Identified in U.S. Patent Application No. 09/823,196 and Their Stable Oxidation States

Metal	Elemental Symbol	Stable Oxidation States
Cerium	Ce	3⁺, 4⁺
Praseodymium	Pr	3⁺, 4⁺
Neodymium	Nd	3⁺
Promethium	Pm	3⁺
Samarium	Sm	3⁺, 2⁺
Europium	Eu	3⁺, 2⁺
Gadolinium	Gd	3⁺
Terbium	Tb	3⁺, 4⁺
Dysprosium	Dy	3⁺
Holmium	Ho	3⁺
Erbium	Er	3⁺
Thulium	Tm	3⁺, 2⁺
Ytterbium	Yb	3⁺, 2⁺
Lutetium	Lu	3⁺
Aluminum	Al	3⁺
Titanium	Ti	4⁺, 3⁺
Yttrium	Y	3⁺
Zirconium	Zr	4⁺
Lanthanum	La	3⁺
Hafnium	Hf	4⁺
Tantalum	Ta	5⁺

Further, with respect to the addition of the proviso to such claims specifying that **at least two of "x" are different**, such amendment is fully supported in the present specification by the formula $M(NR^1R^2)_x$, disclosed therein, wherein the composition may be $Zr(NMe_2)_2(NPr_2)_2$, or $Zr(NEt_2)_2(NPr_2)_2$ (page 14 first paragraph). as it is necessarily inherent in the compositions that "x" is 4 and at least two of "x" are different. Both compositions have "x" = 4 and at least two of "x" are different.

Based on the foregoing, such amendment introduces no new subject matter as such amendment introduces only that which is inherent in the disclosed compositions.

Rejection of Claims Under 35 U.S.C. § 102(b) and § 102(e)

In the July 9, 2002 Office Action the Examiner rejected, claims 1-12, 16 and 37 under 35 U.S.C. § 102(e) as being anticipated by U.S. Patent No. 6,159,855 issued to Brian A. Vaartstra, (hereinafter referred to as "Vaartstra") and claims 1-7, 11-12 and 37 under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent No. 5,139,825 issued to Roy G. Gordon et al., (hereinafter referred to as "Gordon". Such rejections of the claims are traversed in application to the claims as now amended, and in light of the ensuing remarks.

Patentable Distinction of Claims 1-5, 8-12, 16 and 37 Over the Art

Independent claims 1 and 37 have been amended to recite the limitation:

x is from 1 to 5, with the proviso that at least two of x are different.

The CVD precursor composition of the present claims is therefore delimited over both Vaartstra and Gordon, which describe metalloamides having amine groups, which do not vary within a particular metal center.

Vaartstra is directed to organometallic precursors useful for chemical vapor deposition of multi-metallic films. At least two organometallic precursors are combined in a liquid or vapor state and deposited on a substrate. The precursors comprise at least one amino group such that at least two N-R bonds exist for each precursor molecule. R is disclosed as H or carbon. (See column 4, lines 54-57).

Gordon is directed to transition metal amido compounds for depositing transition metal nitride thin films by chemical vapor deposition. The metal amido compounds contain a dialkylamido or a cyclic-amido functional group. (See Column 1, lines 36-39). Three compounds are disclosed, specifically, tetrakis(piperidine) titanium, tetrakis(dimethyl)amido titanium, $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$, and tert-butyl tris(dimethylamido) titanium, $\text{Ti}[\text{N}(\text{CH}_3)_2]_3[\text{CH}_3]$.

According to 35 U.S.C. §102(b) and (e), the reference must teach every aspect of the claimed invention either explicitly or impliedly.

Concerning Vaartstra, the only pertinent teachings for the metalloamide compositions are set out at column 6, lines 19 to 56, as compositions comprising amino groups bonded to a metal center where the particular amino group does not vary within a metal center.

At column 4, lines 10-31, Vaartstra teaches preferred metals as Groups IA, IIA, IIIA, IVA and the transition metals. Vaartstra defines the transition metals as encompassing elements of atomic number 21 through 30 (scandium through zinc), 39 through 48 (yttrium through cadmium), 57 through 79 (lanthanum through gold) and all elements from atomic number 89 (actinium) on.

Vaartstra's compositions include a metal from the list above and an amino group, wherein each amino group comprises at least two N-R bonds where R is disclosed as H or carbon. (See column 4, lines 54-57).

The listing of metals and potential N-R combinations is so extensive and particularized with respect to the Periodic Table, being identified as Groups IA, IIA, IIIA, IVA and the transition metals, as to logically be construed as exclusive in character of other amino combinations. Vaartstra does not identify metalloamide compounds having varying amino ligands bonded to a single metal center. It can only be concluded that the metalloamides disclosed in Vaartstra are taught to be constituted with the specific amino groups disclosed therein, to the exclusion of varying the amino groups.

Neither Vaartstra nor Gordon provides express, implied, or extrapolative basis for a metal "M" having an oxidation state of "x" where "x" is equivalent to the number of amine ligands bonded to the metal center, and where **"x is from 2 to 5, with the proviso that at least two of x are different"** as required by applicant's amended independent claims 1 and 37.

Applicant's present claims exclude the metalloamide species taught by Vaartstra and Gordon, from the scope thereof. Both Vaartstra and Gordon are silent as to metalloamide compounds having different amine groups bonded to a single metal center and as such the present claims 1 and 37 patentably distinguish over Vaartstra and Gordon, as do claims 2-5, 8, 11, 12 and 16 (directly dependent under claim 1) and claims 9 and 10 (indirectly dependent under claim 1).

Based on the foregoing evidence, applicant respectfully requests the Examiner withdraw the rejections under 35 U.S.C. §102(b) and §102(e) of claims 1-5, 8-12, 16 and 37 in favor of a Notice of Allowance.

Accordingly, all pending claims 1-5, 8-12, 16, 37 and 86 are patentably distinguished over the art, and now are in form and condition for allowance.

Petition for Three Month Extension of Time Under 37 C.F.R. § 1.136

Petition hereby is made under the provisions of 37 C.F.R. § 1.136 for a three month extension of the term for response to the July 7, 2002 Office Action in the above-identified patent application, extending the term for response to January 9, 2002.

Upon entry of this Petition, the term for response is extended to expire January 9, 2002.

Fees Due and Payable

In connection with the entry of this amendment, please deduct the amount of \$930 as the fee due for a one month extension of time under 37 C.F.R. § 1.17(a)(3) in response to the July 9, 2002 Office Action, from Deposit Account No. 50-0860 of Advanced Technology Materials Inc.

In connection with the addition of independent claim 86, no net addition of independent claims has been made beyond the number for which payment previously has been made. Accordingly, no added claims fee is due. If it nonetheless is determined that any additional fee or charge is payable in connection with the entry of this Amendment, please charge any deficiency to Deposit Account No. 50-0860.

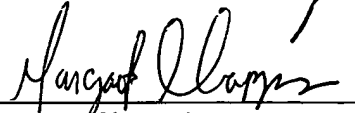
CONCLUSION

In view of the foregoing arguments, it is respectfully submitted that claims 1-5, 8-12, 16, 37 and 86 are now pending in the application are in form and condition for allowance.

The Examiner is therefore requested to take cognizance of the claims as amended herein, and to responsively issue a Notice of Allowability and Notice of Allowance for such claims 1-5, 8-12, 16, 37 and 86.

In the event that any issues remain outstanding, incident to the formal allowance of the application, the Examiner is requested to contact the undersigned agent at (203) 794-1100 ext. 4184 to discuss their resolution, in order that this application may be passed to issue at an early date.

Respectfully submitted.



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Appendix A
Marked-up Version of Claims in U.S. Application Serial No. 09/823,196

The claims have been amended as follows:

1. (AMENDED) A CVD precursor composition for forming a thin film dielectric on a substrate, such precursor composition including at least one metalloamide source reagent compound of the formula:



wherein M is selected from the group consisting of: Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti, Al; N is nitrogen each of ~~R¹ and R²~~ R¹ and R² is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, C₁-C₈ perfluoroalkyl, and alkylsilyl; and x is from 2 to 5 the oxidation state on metal M, with the proviso that at least two of x are different.

2. (AMENDED) The CVD precursor composition according to claim 1, wherein at least one of x is NMe₂, R¹ and R² are methyl.

3. (AMENDED) The CVD precursor composition according to claim 1, wherein at least one of x is NEt₂, R¹ and R² are ethyl.

4. The CVD precursor composition according to claim 1, wherein M is Zr.

5. The CVD precursor composition according to claim 1, wherein M is Hf.

Claims 6 and 7 are cancelled.

8. The CVD precursor composition according to claim 1, wherein the precursor composition further comprises a solvent medium selected from the group consisting of: ethers, glymes, tetraglymes, amines, polyamines, alcohols, glycols, aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, cyclic ethers and combinations of two or more of the foregoing.

9. (AMENDED) The CVD precursor composition according to claim ~~7~~ 4, wherein the precursor composition further comprises a solvent medium selected from the group consisting of: ethers, glymes, tetraglymes, amines, polyamines, alcohols, glycols, aliphatic hydrocarbon

solvents, aromatic hydrocarbon solvents, cyclic ethers and combinations of two or more of the foregoing.

10. (AMENDED) The CVD precursor composition according to claim 9 ~~8~~, wherein the solvent is octane.

11. The CVD precursor composition according to claim 1, wherein the metalloamide source reagent compound is injected by liquid delivery into a chemical vapor deposition chamber.

12. The CVD precursor composition according to claim 1, wherein the metalloamide source reagent compounds is delivered by bubbler into a chemical vapor deposition chamber.

Claims 13 - 15 are cancelled.

16. The CVD precursor composition according to claim 1, wherein the precursor composition comprises multiple metalloamide source reagent compounds.

Claims 17-36 are cancelled.

37. (AMENDED) A CVD precursor composition for forming a thin film dielectric on a substrate, such precursor composition including a vapor source reagent mixture including a metalloamide source reagent compound of the formula:



wherein M is selected from the group consisting of: Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti, Al; N is nitrogen; each of ~~R1 and R2~~ R¹ and R² is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, C₁-C₈ perfluoroalkyl, and alkylsilyl; and x is from 2 to 5 ~~the oxidation state on metal M, with the proviso that at least two of x are different.~~

Claims 38 – 85 are cancelled.

Please add the following new claim:

86. (NEW) A CVD precursor composition for forming a thin film dielectric on a substrate, such precursor composition including a metalloamide source reagent compound selected from the group consisting of: $\text{Zr}(\text{NMe}_2)_2(\text{NPr}_2)_2$, and $\text{Zr}(\text{NEt}_2)_2(\text{NPr}_2)_2$.

Appendix B
Marked-up Version of Paragraph Amendments in U.S. Application Serial No. 09/823,196

Please replace paragraph 1, page 27, with the following paragraph:

Hafnia films were grown with the precursors listed in Table I. Precursor solutions were prepared at 0.1M Hf in octane. Substrate of (100) Si was prepared with an SC1 treatment followed by dilute HF to remove any SiO₂ on the surface. The generic process conditions for the experiments are shown in Table II. Initially, films were grown at 550°C under three different reactive gas conditions: Ar, N₂O and O₂. Results described below indicated that N₂O was the preferred ambient. A pressure-temperature matrix was performed for each precursor using the N₂O ambient as shown in Figures 2A and 2B. Figures 2A and 2B show the process space experiments for TDEAHf and TDMAHf precursors, where the various experiments are identified as GXXX. At the end, a film targeting 50Å was grown from each precursor to be used for TEM examination of the interface with Si.

Please replace paragraph 1, page 30, with the following paragraph:

Silica films were grown with the silicon precursors listed in **Error! Reference source not found.**, TDEASi and TDMASi. Precursor solutions were prepared at 0.1M Si in octane. Substrates of (100) Si were prepared with an SC1 treatment followed by dilute HF to remove any native SiO₂. The generic process conditions for the experiments are shown in **Error! Reference source not found.** Results from the growth of hafnia films encouraged us to center these initial experiments on growth in an N₂O atmosphere although growth in O₂ or other oxidizer could be used at temperatures at or below 500°C. A limited pressure-temperature matrix was performed for each Si precursor using the N₂O ambient as shown in Figure ~~10A and 10B~~ 7A and 7B, where the various experiments are identified as GXXX.

Please replace paragraph 3, page 31, with the following paragraph:

Growth rates of SiO_2 were less than $3\text{\AA}/\text{min}$ under all conditions as shown in Figure ~~11~~ 8 and Figure ~~12~~ 9. There is some indication that the TDEASi may form silica films a little bit more readily, however, none of the growth rates are sufficient for the two precursors under the instant conditions.

Please replace paragraph 4, page 31, with the following paragraph:

The growth of SiO_2 with only the TDEAHf, as measured by the subtraction of ellipsometric thickness from XRF thickness (shown in Figure ~~13~~ 10) was greater than that from the TDEASi precursor alone. ~~(Figure 11)~~ Films grown from the precursor mixture (TDEAHf+TDEASi) showed still higher SiO_2 growth rates as shown in Figure ~~14~~ 11. This increased growth rate ~~compared to Figure 11~~ is unexpected and should be quite useful for the growth of hafnium silicate films of uniform Hf:Si composition through the thickness of the film.